

Miniaturized GC/MS instrumentation for *in situ* measurements: micro gas chromatography coupled with miniature quadrupole array and Paul ion trap mass spectrometers

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ABSTRACT

Miniaturized chemical instrumentation is needed for *in situ* measurements in planetary exploration and other spaceflight applications where factors such as reduction in payload requirements and enhanced robustness are important. In response to this need, we are continuing to develop miniaturized GC/MS instrumentation which combines chemical separations by gas chromatography (GC) with mass spectrometry (MS) to provide positive identification of chemical compounds in complex mixtures of gases, such as those found in the International Space Station's cabin atmosphere. Our design approach utilizes micro gas chromatography components coupled with either a miniature quadrupole mass spectrometer array (QMSA) or compact, high-resolution Paul ion trap. Key design issues include high sensitivity, good MS resolution (0.5 amu FWHM or better), low power, robustness, low GC flow rates to minimize vacuum-pumping requirements, and the use of a modular approach to adapt to different environments. Among the potential applications for such instrumentation are *in situ* detection of astrobiology signatures (using air sampling or ground-drilling techniques), planetary aeronomy, and monitoring of cabin air during long duration human flight.

Key words: GC/MS, gas chromatography, mass spectrometry, miniature instrumentation, MEMS, *in situ* measurements

INTRODUCTION

Miniaturized chemical instrumentation is needed for *in situ* measurements in planetary exploration and other spaceflight applications where factors such as reduction in payload requirements and enhanced robustness are important. In response to this need, we are continuing to develop miniaturized GC/MS instrumentation which combines chemical separations by gas chromatography (GC) with mass spectrometry (MS) to provide positive identification of chemical compounds in complex mixtures of gases, such as those found in the International Space Station's cabin atmosphere. Our design approach utilizes micro gas chromatography components coupled with either a miniature quadrupole mass spectrometer array (QMSA) or compact, high-resolution Paul ion trap. Key design issues include high sensitivity, good MS resolution (0.5 amu FWHM or better), low power, robustness, low GC flow rates to minimize vacuum-pumping requirements, and the use of a modular approach to adapt to different environments. Among the potential applications for such instrumentation are *in situ* detection of astrobiology signatures (using air sampling or ground-drilling techniques), planetary aeronomy, and monitoring of cabin air during long duration human flight.

1. BACKGROUND

In situ exploration of the solar system to identify its early chemistry and to look for compelling evidence of astrobiology will require new enabling technology for chemical analysis. Here, identification and characterization of biomarkers of extinct or extant life and early pre-biotic chemistry in the solar system will be of special importance. GC/MS (gas chromatography combined with mass spectrometry detection) provides an especially powerful analytical tool for the identification of unknown chemical compounds. While mass spectrometry alone provides important capability for identifying the chemical structures of unknown compounds from observations of their ion fragments, it suffers from inherent difficulty in dealing with mixtures, especially when compounds of interest may be present at low levels. Combining mass spectrometry with gas chromatography (GC) provides rapid separation of even complex chemical mixtures *before* they are detected by the MS. This "pre-processing" of the sample using GC presents the MS with a sequence of pure compounds for detection and identification, allowing even trace level species to be detected in the presence of complex backgrounds. This makes GC/MS arguably the most powerful general purpose technique for chemical analysis. Here, the signature-like mass spectrum for each compound can be used to identify specific structural features of the molecule, and when coupled with characteristic GC retention times provides virtually positive identifications. Given sufficient S/N, it is also often possible to infer the isotopic composition (and ratios) of resulting ion fragments produced for each compound, further enhancing the scientific value of *in situ* GC/MS measurements.

To be useful for *in situ* astrobiology or other spaceflight applications, GC/MS instrumentation must be both miniature and rugged, while using very little power and other consumables. Fortunately, instrument robustness is enhanced by miniaturization due to size scaling factors since instrument mass decreases more rapidly than cross-sectional areas, increasing the relative strength of components. Besides reducing power requirements and the use of consumables, small size may significantly decrease the amount of sample that is required, allowing other supporting systems to be scaled down. Miniaturization is especially favorable in the case of gas chromatography separations for GC/MS applications. Here, the use of short micro-bore columns makes separations much faster without adversely effecting resolution, while at the same time greatly reducing flow rates from the GC column into the mass spectrometer. This minimizes vacuum pumping requirements and carrier gas consumption, allowing the overall weight and power of the system to be significantly reduced.

In situ chemical measurements for astrobiology and other spaceflight applications highlight the need for the high level of positive identification of chemical compounds offered by GC/MS. This is especially important since re-measurement by alternative techniques for confirmation may not be feasible. It also may not be possible to anticipate all chemical species that are observed, and important species may be present only at trace levels where they could be masked by complex chemical backgrounds. These considerations help make GC/MS the method of choice for *in situ* chemical measurements. While gas chromatography has played a significant role in previous planetary missions¹ and a variety of miniature mass analyzers have been developed,² weight and power requirements have so far precluded the use of GC/MS in planetary missions, with the exception of a large and complex (10s of kg) Pyrolysis/GC/MS system for the upcoming Cassini/Huygens Probe into the atmosphere of Saturn's moon Titan.³ A new generation of miniaturized low power GC/MS instrumentation will be needed to fill this technology gap. Here, MEMS technology and other approaches to miniaturization can dramatically increase the robustness of systems and components, reduce life-cycle costs and minimize the need for redundancy.

2. MINIATURE GC/MS INSTRUMENTATION

Our technical approach in developing miniature GC/MS instrumentation is based on the use of a MEMS-based GC injector and micro-bore capillary columns for performing the separations, coupled with the new miniature mass spectrometer technology being development at NASA/JPL.^{4,6} The silicon micro-machined injection valve we employ is shown in Figure 1 and is about 3 x 2.5 cm in size. The valve has a sample loop with a volume of 15 μ L (micro-liters), which can provide precise, programmable gas sample injections of 0.5-15 μ L. Such valves have been tested for over 2.5 million analysis cycles without signs of wear. The injection valve itself is operated pneumatically from the carrier gas supply and thus does not directly require power. A key feature of this design is that the sample loop is first thoroughly flushed with fresh sample, the sample then pressurized to the GC column head pressure (in the sample loop), followed by injection of a very small plug of gaseous

sample at carrier gas pressure onto the GC column. This is important because volumes must be carefully controlled to maintain low flow rates to the MS detector in a GC/MS micro-instrument configuration.

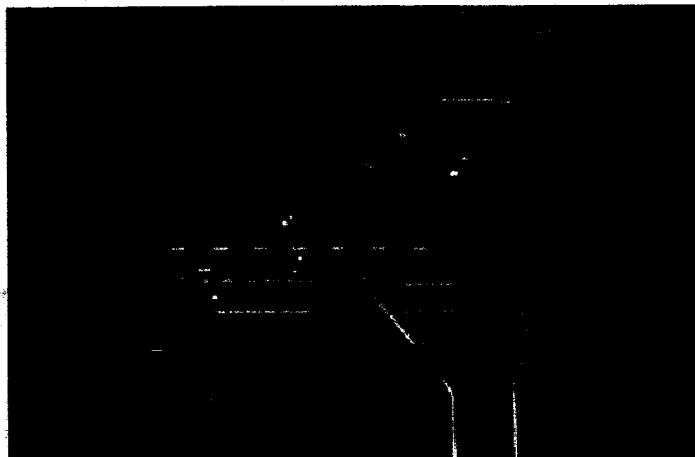


Figure 1: Silicon micro-machined GC injector (see text).

Gas flow rates from the GC into the MS are a key design issue for miniature GC/MS systems due to the need to keep vacuum pumping requirements and power usage low. Flow rates for the GC/QMSA instrument range from 10 to a few hundred $\mu\text{L}/\text{min}$, much lower than typical laboratory GC flow rates of 2-30 mL/min . Such flow rates can be calculated using the Poiseuille equation, allowing the flow rate (at some standard pressure) to be calculated from inlet and outlet pressures of the GC column, internal radius R and length L of the column, and carrier gas viscosity, η . In GC/MS applications, since the outlet of the column is in the pumped region of the MS, the outlet pressure will be maintained at zero.

$$\text{Flow Rate} = \frac{\pi R^4}{8 \eta L} (P_{\text{inlet}} - P_{\text{outlet}}) \frac{P_{\text{inlet}} + P_{\text{outlet}}}{2 P_{\text{standard}}}$$

The primary mass spectrometer detector we have employed in our GC/MS work is the QMSA (quadrupole mass spectrometer array) shown in Figure 2. This miniature high resolution, quadrupole array has been certified as a NASA flight instrument and has been deployed on the International Space Station. The QMSA itself is comprised of 16 rods in a 4×4 array (each 2.5 cm in length) and utilizes a single ionizer for the MS array.⁴ Detection sensitivity is 2×10^{12} counts/torr-sec, with a mass resolution $m/\Delta m$ of 600 over a range of 1-300 amu. The present configuration of the vacuum housing of this instrument provides a direct access port to the ionizer via a 1.33 inch stainless steel vacuum conflat flange, which provides a simple interface to the GC column via a standard 1/16" compression fitting.

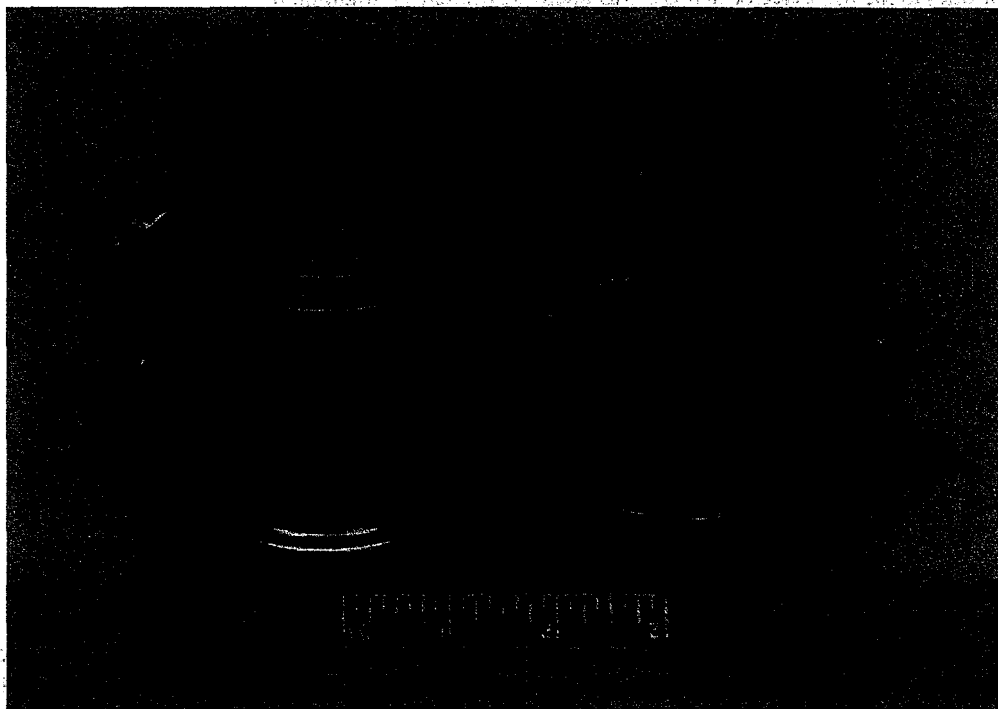


Figure 2. Quadrupole mass spectrometer array.

A simplified overview of the GC/MS system is shown in Figure 3. First, a sample is drawn through the 15 μL sample loop of the MEMS GC injector by a miniature sampling pump. The injector is pneumatically operated by carrier gas pressure using miniature solenoid valves (not shown), and a sample plug of 0.5-15 μL is injected onto the GC column. A flow of carrier gas (typically helium) carries the sample through the column. After separation on the GC column, compounds for analysis pass into the miniature mass spectrometer for mass analysis and detection.

The breadboard GC/QMSA itself is shown in Figure 4. A Tedlar gas sampling bag is shown on the left, along with a miniature carrier gas regulator, pneumatic control valves and sampling pump. The MEMS injector (lower center, shown covered with foil insulation) is heated, as is the sampling line connected to the Tedlar bag. From the injector the sample passes into the GC column assembly (lower right), and then into the QMSA (upper right).

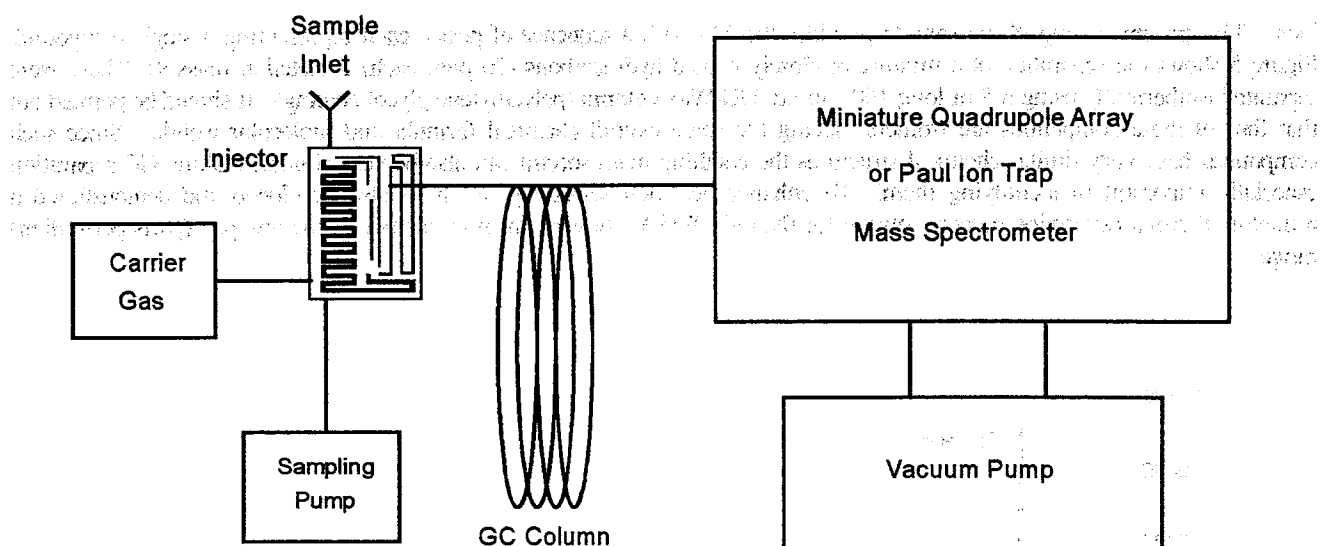


Figure 3. Overview of GC/MS instrumentation design.



Figure 4. GC/QMSA instrumentation configuration.

Typical results for the GC/QMSA are shown in the ion chromatogram in Figure 5. This illustrates how gas chromatography provides separation of even complex chemical mixtures based on differences in the time required for different chemical components to flow through and exit the length of the GC column under controlled conditions. The separation arises from differing interactions of components in the mixture with thin polymeric coatings on the walls inside the column, causing those which interact more strongly to spend less time in the carrier gas flowing through the column and reach the detector

later. This pre-processing of the sample provides the MS with a sequence of peaks, each representing a single compound. Figure 5 shows the separation of a mixture of closely related hydrocarbons (70 ppm each) detected at mass 91. These were separated isothermally using a 5 m long 100 μm i.d. DB-Wax column (polyethylene glycol coating). It should be pointed out that four of these compounds are isomers, having the same overall chemical formula and molecular weight. Since such compounds have very similar chemical structures the resulting mass spectra can also be very similar, making GC separation especially important in identifying them. To enhance detection sensitivity, we have also developed and demonstrated a miniature thermal desorption preconcentrator for the GC/QMSA, allowing measurements into the low ppb (parts-per-billion) range.

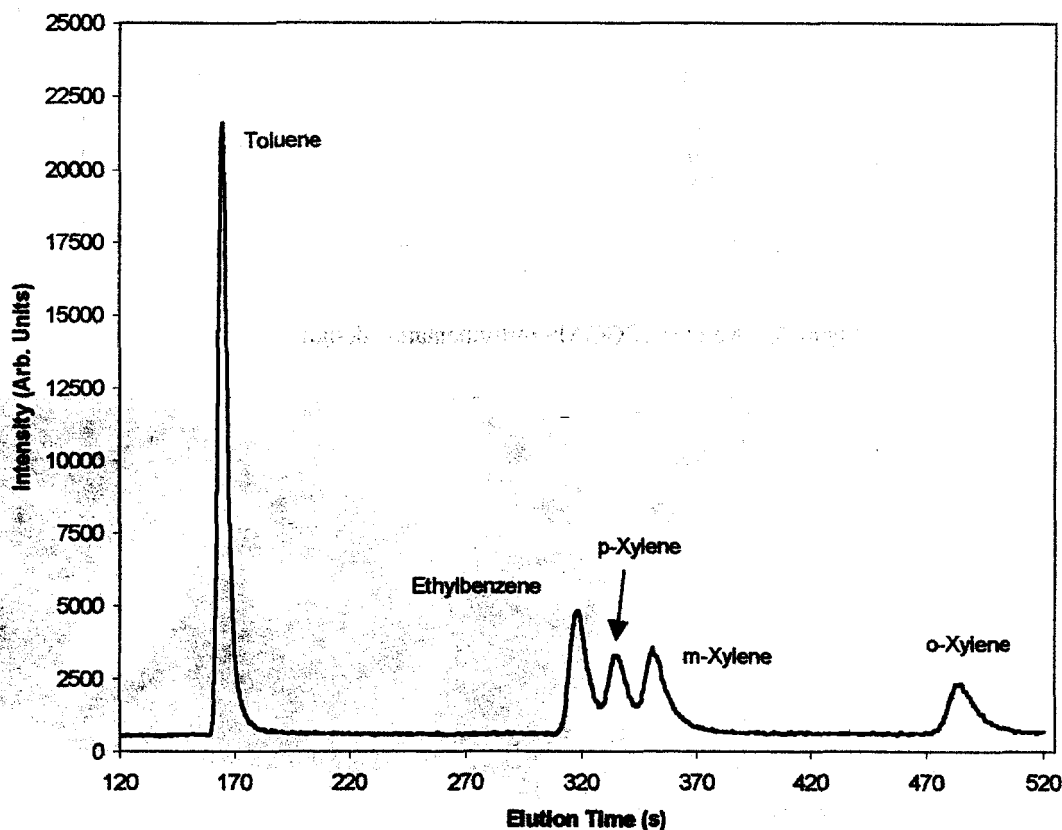


Figure 5. Example GC/QMSA results for a hydrocarbon mixture.

Mass spectrometric detection in GC/MS provides important capability for resolving isotopic ratios even at trace levels, since the GC separation removes background interferences. Example measurements with the GC/QMSA for 50 ppm of Ne in CO_2 to simulate a Venus-like atmosphere, were made using a 3 m long 320 μm i.d. Carboxen PLOT column (carbon molecular sieve coating, porous layer open tubular) coupled with a 50 μm i.d. flow restrictor. The results, shown in Figure 6, give relative abundances of $91.0 \pm 1.0\%$ for ^{20}Ne and $9.1 \pm 0.3\%$ for ^{22}Ne in agreement with standard values. The isotopic composition of specific chemical compounds (and their ratios) can also be determined where S/N is adequate, since chemically identical compounds will co-elute. Since mass to charge ratios of the resulting ion fragments can be observed, determining specific sites on a molecule where chemical reactions with an isotope tagged reactant may be possible.

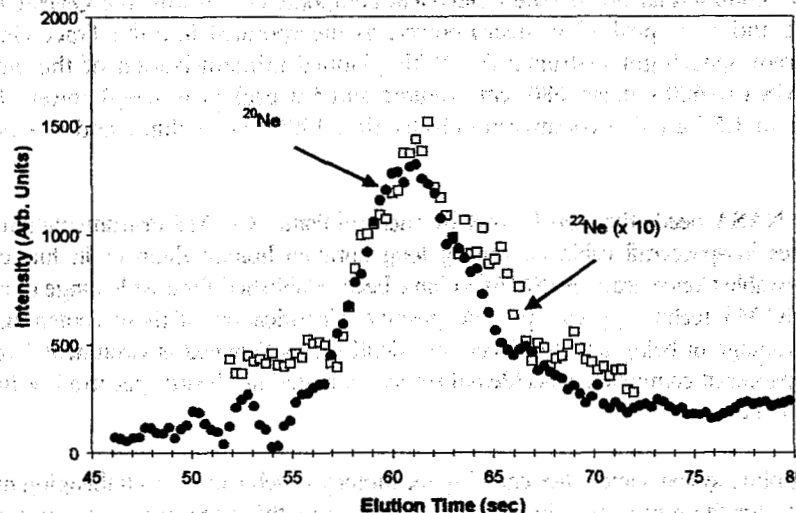


Figure 6. Example GC/QMSA results for neon isotopes.

A miniature hyperboloidal Paul ion trap mass spectrometer has recently been developed as an alternative high resolution, extended mass range detector for the GC/MS.⁶ This is shown mounted on a 6" conflat flange in Figure 7. The overall size of the Paul ion trap is about 5 cm in diameter, with trap radius $r_0 = 1$ cm and mass range to 10,000 amu. With a sensitivity of 2×10^{14} counts/torr-sec it is about 100x more sensitive than the QMSA, and because it operates in a radio-frequency only mode and no dc is required, simplicity and low power operation are possible. This makes the Paul ion trap well suited for autonomous operation in harsh environments requiring low power, low weight, and low volume.

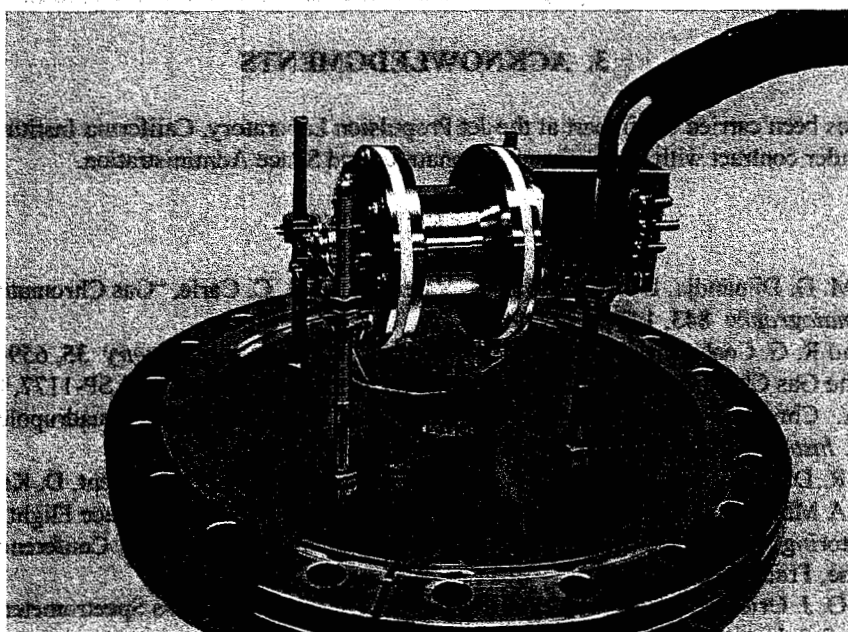


Figure 7. Miniature Paul ion trap mass spectrometer.

The mass and power consumption of the present GC/QMSA breadboard instrumentation are 1.9 kg and 16 watts, based on the use of commercial off-the-shelf electrical components. Of this, the QMSA itself comprises 1.7 kg mass, 2000 cm³ volume and 15 w peak (2 w sleep) power, as incorporated into the Trace Gas Analyzer (TGA) for astronaut EVA (the current spaceflight instrument). With planned miniaturization of the electronics, it should be possible to reduce the QMSA to 600 g mass, 680 cm³ volume and 5 w peak (1 w sleep) power. In its present form, the Paul ion trap has a mass of 1.5 kg using commercial electronics, 1900 cm³ volume and 8 w peak (1 w sleep) power consumption.

Other important NASA needs that can be met by such miniature GC/MS instrumentation include environmental monitoring of contaminants in spacecraft cabin air during long duration human flight or in future space habitats. Here, Spacecraft Maximum Allowable Concentrations (SMACs) have been established for a wide range of compounds down to low ppb levels. Miniature GC/MS technology can provide positive identification of these contaminants. Furthermore, this approach provides the advantage of being able to detect and identify unanticipated environmental contaminants that might arise from outgassing of spacecraft components, accidental release of materials aboard spacecraft or in habitats, or during the extraction of planetary resources.

Miniaturized sampling systems and other enabling technology which can meet challenging mass, volume and power constraints will be required for these miniature instruments. To address this need, we are developing a variety of different "front ends" for sample collection and pre-processing which are designed to interface with miniature GC/MS technology or other *in situ* instrumentation. These include:

- A miniaturized, very low power thermal desorption preconcentrator
- Miniature liquid water extraction systems designed to function in micro-gravity environments for both dissolved gases and trace level organic compounds
- A micro-sampling probe and low power programmable thermal desorption/pyrolysis inlet system for *in situ* astrobiology-related measurements in soils and ice
- A high pressure micro-sampling inlet system for *in situ* measurements in deep subsurface environments, since the integrity of samples may be compromised by degassing of volatile components if brought to the surface.

Together with the new generation of miniaturized instrumentation currently under development, these sampling systems will address needs for *in situ* detection of astrobiology signatures and for measurements in extreme earth environments.

3. ACKNOWLEDGMENTS

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